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(54) TITANIC ACID LITHIUM POWDER AND ITS USE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide lithium titanate powder to improve tap density and reduce paint viscosity when electrode mix is kneaded, an electrode for a lithium secondary battery using the lithium titanate powder and a high performance lithium secondary battery using the electrode.

SOLUTION: The lithium titanate powder in the invention is coated with polyol and/or coupling agent on its surface, $Li_4Ti_5O_{12}$ is used as its main component and its tap density is 0.75 g/ml or more. The lithium secondary battery is produced by using said lithium titanate powder as an electrode.

[Claim(s)]

[Claim 1] Lithium titanate fine particles which are fine particles consisting of $Li_4Ti_5O_{12}$ as a principal component, wherein herein $Li_4Ti_5O_{12}$ is a principal component, and the surface of these fine particles is covered with polyol and/or a coupling agent.

[Claim 2] Lithium titanate fine particles according to claim 1 wherein tap density of said fine particles is 0.75g/ml or more.

[Claim 3] The electrode for cells characterized in that fine particles according to claim 1 or 2 are used as a positive electrode or a negative-electrode active material.

[Claim 4] The lithium secondary battery using the electrode for cells according to claim 3.

[Claim 5] The lithium secondary battery wherein lithium titanate fine particles according to claim 1 or 2 are used as positive active material, and metal Li is used as as a negative electrode, a charge/discharge voltage thereof in a charge and discharge test being 1.4-1.6V, and an initial discharge capacity being 150 or more mAh/g.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to lithium titanate fine particles that is useful as an active material of a lithium secondary battery, and the lithium secondary battery using the lithium titanate fine particles.

[0002]

[Description of the Prior Art] Although the lithium secondary battery has progressed as a power source for a cellular phone or notebook computers from the height of the energy density, the cell which is the power source has also come to be further asked for small and high capacity-ization with small [of a personal digital assistant device], and lightweight-izing by advance of IT technique in recent years.

[0003] When the lithium titanate which is a lithium titanium multiple oxide has Li4Ti 5O12 in a typical thing and it considers as the active material of a lithium secondary battery, it has the electrical potential difference of 1.5V on lithium criteria, and it is the description that cycle degradation is small long lasting. Moreover, it has a track record as an active material of the small lithium secondary battery for clocks, and is

observed also as an active material for large-sized cells from the description that expansion and contraction can be disregarded on the occasion of charge and discharge. This ingredient has also opened the use side as a negative-electrode active material besides as positive active material use, and that future is expected.

[0004] It is proposed by there being the approach of enlarging electric capacity of the active material itself for small [of a cell], and high-capacity-izing, for example, permuting some lithium titanates by WO 99/03784 in a proton, and hydrogenating that the charge-and-discharge capacity exceeding geometric capacity is obtained. However, about the approach of raising the pack density of an active material and enlarging electric capacity, the report is not yet made.

[0005]

[Problem(s) to be Solved by the Invention] This invention is to offer [manufacturing the lithium titanate fine particles by which surface coating was carried out by polyol and/or the coupling agent, and] the lithium secondary battery using these lithium titanate fine particles, in order to improve the lithium secondary battery property of using lithium titanate.

[0006]

[Means for Solving the Problem] the lithium titanate fine particles which carried out surface coating by polyol and/or the coupling agent as a result of repeating research wholeheartedly that this invention persons should attain the above-mentioned purpose -- tap density -- improving -- an electrode -- it turned out that the coating viscosity when kneading a mixture can be reduced. Moreover, a header and this invention were completed for the lithium secondary battery which used the fine particles of this lithium titanate as an active material showing the outstanding charge-and-discharge property.

[0007] That is, the lithium titanate fine particles of this invention are fine particles which use Li4Ti 5O12 as a principal component, and the front face of these fine particles is characterized by being covered with polyol and/or a coupling agent.

[0008] Moreover, in the lithium titanate of this invention, the tap density of the fine particles may be 0.75g/ml or more.

[0009] Moreover, the electrode for cells using said lithium titanate fine particles as a positive electrode or a negative-electrode active material can be offered.

[0010] Moreover, the lithium secondary battery using said electrode for cells can be offered.

[0011] Furthermore, it is the lithium secondary battery which uses said lithium titanate fine particles as positive active material, and uses Metal Li as a negative electrode, and ** and discharge voltage can offer the lithium secondary battery 1.4-1.6V, and whose initial discharge capacity are 150 or more mAh/g.

[0012]

[Embodiment of the Invention]

The lithium titanate fine particles of this invention is characterized in that each particle thereof is surface-coated with polyol and/or the coupling agent, and the principal component is $Li_4Ti_5O_{12}$, and preferably the tap density thereof is 0.75g/ml or more preferably. The electrode active material for lithium secondary batteries which show excellent charge-and-discharge properties mentioned later can be prepared within the scope of this tap density.

[0013]

The lithium titanate fine particles used as the base before carrying out surface coating can be typically manufactured according to the process comprising a step of mixing raw materials uniformly in water, and a step of drying the mixture, and the step of heat-treating the dried matter.

[0014]

First, a lithium hydroxide, a lithium hydroxide monohydrate, lithium oxide, a lithium hydrogen carbonate, a lithium carbonate, etc. as a lithium raw material is mixed or dissolved in water. Titanium oxide is added to the liquid so that the atomic ratio of Li and Ti becomes 4:5. The titanium oxide to be used is preferably an anatase-type titanium dioxide or hydrous titanium oxide. About an anatase-type titanium dioxide, at least 95% or more is required for purity, and it is 98% or more of thing preferably. When purity is less than 95%, since the capacity per unit active material falls, it is not desirable. Becoming the purity of the above-mentioned range, when it calcinates and considers as an anatase mold titanium dioxide about water titanium oxide, the standard of the purity of the water titanium oxide before baking in this case is 90% or more.

[0015]

While fulfilling the conditions of the aforementioned atomic ratio, as for the slurry concentration of mixed liquor, it is desirable that Li raw material is 0.48-4.8mol/L, and titanium oxide is 0.60-6.00mol/L. When concentration is higher than these ranges, strong stirring force for uniform mixing is required and it causes troubles such as piping lock out at the time of desiccation, and it follows that it is not desirable. Since an evaporation moisture content will increase and desiccation cost will go up, if concentration is lower than the aforementioned range, and it follows that it is not desirable. The desiccation approach may not be limited to a specific process, for example, spray drying, fluidized bed drying, rolling granulation desiccation, or freeze drying, which may be employed alone or in combination.

[0016]

The obtained dried matter is heat-treated in atmospheric air, and the lithium titanate particle whose mean diameter is 0.1-50 μm is obtained. Heat treatment conditions are generally from 1 to 10 hours at 700-1000℃, and preferably from 5 to 10 hours at 800-900℃. At the temperature of less than 700℃, the reaction of titanium oxide and a lithium compound is insufficient, on the other hand, at the temperature of more than 1000℃, sintering of lithium titanate takes place notably and a cell property worsens, and it is not desirable.

[0017]

The lithium titanate granulated as described above is subjected to the surface coating process by polyol and/or the coupling agent.

[0018]

Although the class of polyol is not especially limited, it is independent selected from pentaerythritol, triethyrol ethane, trimethylol propane, etc. or a combination thereof. The polyol is dissolved in a solvent that can dissolve the polyol, and after the dissolution, the solution and the above granulated lithium titanate are mixed. The addition amount of polyol is 0.2 to 2.0 wt%, and preferably 0.5 to 1.5 wt% with respect to lithium titanate as the base. If there are few additions than 0.2 wt%, improvement in sufficient tap density will not be obtained, and since there is also little reduction effectiveness of coating viscosity, it is not desirable. Moreover, it brings about the fall of discharge capacity and it is not desirable, if the addition is more than 2.0 wt%.

[0019]

After mixing, heat-treatment at 50-200℃, preferably 80-150℃ is carried out. Heat treatment time amount is 1-10 hours, and preferably for 30 minutes to 24 hours. The hydroxyl group on each front face of a particle of lithium titanate and the hydroxyl group in polyol react by this, and an organic layer is formed in a lithium titanate particle front face. The interaction between particles decreases by the organic functional group of a covering organic layer, and it becomes possible to raise tap density of the lithium titanate fine particles in which the organic layer of the polyol origin was formed. Since the reaction of organic layer formation will not advance if said heat treatment temperature is lower than 50 degrees C, and polyol will decompose if higher than 200 degrees C, a desired organic layer is not formed and the effectiveness of the improvement in tap density is not acquired, it is not desirable.

[0020]

Moreover, in case of sintering the lithium titanate used as said base, when crushing processing is required, polyol can be added in the form of solid-state, without dissolving, before the crushing and the crushing processing serves both as fusion and

covering of polyol. According to this method, there is effectiveness which controls improvement in the efficiency of comminution, and the coagulation and agglomeration at the time of grinding.

[0021]

Although especially the class of coupling agent is not limited, a silane coupling agent, a titanium coupling agent, an aluminum coupling agent, etc. can be used, and a silane coupling agent is desirable especially. independent [, for example / in vinyl trichlorosilan a vinyl tris silane, vinyltriethoxysilane, vinyltrimetoxysilane, gamma-methacryloxpropyl trimethoxy silane, gamma-glycidoxypropyltrimetoxysilane, gamma-aminopropyl triethoxysilane, gamma-mercapto propyltrimethoxysilane, gamma-chloropropyltrimetoxysilane, etc.] as a silane coupling agent -- or it can be combined and used. An art mixes said coupling agent with said lithium titanate. the lithium titanate with which the addition of a coupling agent serves as a base -- receiving -- 0.2 to 2.0 mass % -- it is 0.5 to 1.5 mass % preferably. If there are few additions than 0.2 mass %, improvement in sufficient tap density will not be obtained, and since there is also little reduction effectiveness of coating viscosity, it is not desirable. Moreover, it brings about the fall of discharge capacity and is not desirable if [than 2.0 mass %] more.

[0022]

After mixing, heat-treatment at 50-200℃, preferably 80-150℃ is carried out. Heat treatment time amount is 1-10 hours, and preferably for 30 minutes to 24 hours. The hydroxyl group of a lithium titanate particle front face and the functional group of a coupling agent react by this, and a coupling agent is covered by the particle front face. Consequently, the interaction between the particles in lithium titanate fine particles can decrease, and tap density can be raised. Since a coupling agent will decompose if higher [if said heat treatment temperature is lower than 50 degrees C, an unreacted coupling agent will remain and sufficient effectiveness will not be acquired, and] than 200 degrees C, it is not desirable.

[0023] Moreover, it can also be used, combining said polyol and said coupling agent suitably.

[0024] The dispersibility of lithium titanate fine particles by which surface coating processing of this invention was carried out to the inside of the n-methyl-2-pyrrolidone generally at the time of electrode production used can improve, and they can reduce coating viscosity. Since it becomes producible [a coating] by high concentration as a result of coating viscosity's falling, the pack density to a charge collector top improves.

[0025] The coin mold rechargeable battery was produced as a lithium secondary battery which used the lithium titanate fine particles compounded as mentioned

above as positive active material, and used Li metal for the negative electrode, and ** and a spark test were performed. Consequently, when the lithium titanate fine particles of this invention were used, the electrical potential difference in charge and discharge was able to satisfy 1.4-1.6V, and was able to acquire the value with a as high initial discharge capacity as 150 or more mAh/g. Moreover, the capacity of discharge rate 3.0C is 110 or more mAh/g, and the large thing was found out compared with 105 mAh/g in not processing.

[0026]

[Example] Although hereafter explained concretely based on an example and the example of a comparison, this invention is not limited to these examples.

[0027]

[Example 1]

Lithium hydroxide ($LiOH \cdot H_2O$) was dissolved in water by concentration of 12%, and anatase-type titanium dioxide was added to the solution in the amount so that the atomic ratio of Li and Ti was set to 4:5. The mixture was spray-dried at 110℃, and then heat-treatment was carried out at 875℃ for 6 hours to form lithium titanate.

Trimethylol propane solution in ethanol is added to the the lithium titanate, and thne heat-treatment of 1.5 hours was performed at 110 degrees C, and the fine-particles sample was produced. The addition of trimethylol propane was made into 1.0 mass %. The tap density of this sample was measured by the JIS-K-5101 tap method. Moreover, it kneaded for 5 minutes by the high SHIEA mixer at 46.5% of solid content concentration to the N-methyl-2-pyrrolidone after mixing this sample 82 weight section, the acetylene black 9 weight section, and the polyvinylidene fluoride 9 weight section, and the coating was produced. The viscosity of this coating was measured by the Brookfield viscometer.

[0028] Next, the above-mentioned coating was applied so that the thickness after desiccation might become 0.01 g/cm2 with a doctor blade method on aluminum foil. 110 degrees C -- after a vacuum drying and an initial electrode -- the roll press was made 80% to the thickness of a mixture. The positive electrode 3 of the coin cell shown in drawing 1 took after piercing to 2 1cm. In drawing 1 , the separator 5 used the polypropylene porosity film for that from which, as for the negative electrode 4, the electrolytic solution dissolved LiPF6 for the metal lithium plate in the amount mixture of isochore of ethylene carbonate and dimethyl carbonate by one mol / L. Using the coin cell produced by the above, it charged to 1.0V by current density 0.2 mA/cm2, and charged to 3.0V with this current density after discharge, and this cycle was repeated 3 times. Then, it discharged with the current density from which a discharge rate serves as 3.0C. The measurement result of tap density, coating viscosity, and discharge capacity is shown in Table 1.

[0029]

[Example 2] Except having done 0.5 mass % mixing of vinyltriethoxysilane at lithium titanate, it carried out like the example 1 and tap density, coating viscosity, and discharge capacity were measured. A result is shown in Table 1.

[0030]

[Example 3] Except having done 1.0 mass % mixing of vinyltriethoxysilane at lithium titanate, it carried out like the example 1 and tap density, coating viscosity, and discharge capacity were measured. A result is shown in Table 1.

[0031]

[Example 4] Except having done 1.5 mass % mixing of vinyltriethoxysilane at lithium titanate, it carried out like the example 1 and tap density, coating viscosity, and discharge capacity were measured. A result is shown in Table 1.

[0032]

[Example 5] Except having done 2.0 mass % mixing of vinyltriethoxysilane at lithium titanate, it carried out like the example 1 and tap density, coating viscosity, and discharge capacity were measured. A result is shown in Table 1.

[0033]

[Example 6] Except having done 1.5 mass % mixing of gamma-methacryloxpropyl trimethoxy silane at lithium titanate, it carried out like the example 1 and tap density, coating viscosity, and discharge capacity were measured. A result is shown in Table 1.

[0034]

[Example 7] Except having done 1.5 mass % mixing of gamma-aminopropyl triethoxysilane at lithium titanate, it carried out like the example 1 and tap density, coating viscosity, and discharge capacity were measured. A result is shown in Table 1.

[0035]

[The example 1 of a comparison] Except having mixed neither polyol nor a coupling agent to lithium titanate, it carried out like the example 1 and tap density, coating viscosity, and discharge capacity were measured. A result is shown in Table 1.

[0036] As shown in Table 1, tap density of examples 1-4 improves to the example 1 of a comparison, and coating viscosity is also falling. Moreover, examples 1-3 were able to raise a high rate (3.0C) discharge capacity, maintaining a low rate (0.15C) discharge capacity.

[0037]

[Table 1]

[0038]

[Effect of the Invention] As explained above, since the fine-particles front face is covered with polyol and/or a coupling agent, the lithium titanate fine particles of this invention can raise improvement in tap density, the fall of coating viscosity, and the discharge property of a high rate compared with what is not covered.